

1336391

PATENT SPECIFICATION

(11) 1336391

NO DRAWINGS

- (21) Application No. 24372/71 (22) Filed 19 April 1971
 (31) Convention Application No. 15257 (32) Filed 27 Feb. 1970 in
 (33) United States of America (US)
 (44) Complete Specification published 7 Nov. 1973
 (51) International Classification C08F 45/58
 (52) Index at acceptance
 C3P 7C18 7C20B 7C20C 7C20D1 7C20D2 7C8B 7D1A
 7D1C 7D1X



(54) STABILISED COMPOSITIONS

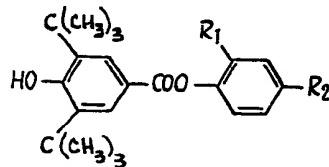
(71) We, CIBA-GEIGY A.G., a body corporate, organised according to the laws of Switzerland, of 4002 Basle, Switzerland, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of stabilising light-sensitive polyolefins; this invention also relates to the stabilised polyolefins.

It is known from U.S. Patents Nos. 3,112,338 and 3,206,431 to use, as light stabilisers, 4-hydroxy-3,5-di-tert.-butylbenzoic acid aryl esters, especially the 2,4-di-tert.-butylphenyl ester. If, however, such compounds are incorporated into organic polymers to protect them against a deterioration of the mechanical and electrical properties, then they have the disadvantage that, under the effect of light, yellowing occurs. Surprisingly, it has now been found that this yellowing can be prevented by the addition of certain 2-hydroxybenzophenones which are known *per se*; for example, from U.S. Patents Nos. 3,006,959 and 3,098,842.

According to the present invention, there is provided a method of stabilising light-sensitive polyolefins, which method comprises incorporating into the polyolefin, in a total amount from 0.2% to 1.2% by weight of the unstabilised polyolefin;

i) from 0.05% to 0.8% by weight of the unstabilised polyolefin of a compound of the formula:



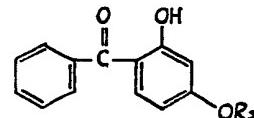
wherein:

R₁ represents a hydrogen atom or a methyl, tert.-butyl or tert.-amyl group; and

R₂ represents a methyl, tert.-butyl, tert.-amyl or tert.-octyl group,

R₁ and R₂ together containing at least 5 carbon atoms; and

ii) from 0.05% to 0.8% by weight of the unstabilised polyolefin of a compound of the formula:



wherein:

R₃ represents a C₈ to C₁₂ alkyl group, preferably an octyl, decyl or dodecyl group.

For reasons of better compatibility, R₁ and R₂ in the compounds of the formula I must together contain at least 5 carbon atoms.

The stabiliser system, according to the invention, is preferably used in fibres, films and sheets, i.e. in thin polymer structures. As a further advantage, it has been shown that the stabiliser system has appreciably better compatibility with the polyolefin than an equal concentration of pure 4-hydroxy-3,5-di-tert.-butylbenzoic acid phenyl ester of the formula I. This better compatibility is particularly clearly shown in the case of the higher light-stabiliser concentrations of 0.4% and above, necessary for thin polymer structures, where, in using the stabiliser system according to the invention, no subsequent efflorescence or exudation of the stabiliser need be feared. Moreover, the stabiliser system, according to the invention, has less inherent colour than the same amount of the previously known 2-hydroxybenzophenones of the formula II, and it has the additional advantage that the attained light stabilisation effect is higher

40

45

50

55

60

65

70

75

than was to be expected on the basis of the purely additive effect of the two components.

In the method according to the invention, 5 0.05 to 0.5% by weight of 4-hydroxy-3,5-di-tert.-butylbenzoic acid phenyl ester and 0.1 to 0.8% by weight of 2-hydroxybenzophenone are preferably used. For the compounds of the formula I, the best embodiment is given by 10 0.05 to 0.25% by weight and by 0.2 to 0.5% by weight for the compounds of the formula II. The sum of the incorporated stabilizers of formulae I and II is preferably, 0.2 to 0.8% by weight with particular preference being given to 0.2 to 0.5% by weight, calculated on 15 the unstabilised substrate.

Valuable 3,5-di-tert.-butyl-4-hydroxybenzoic acid phenyl esters, usable according to the invention, are, e.g.:

- 20 A) 3,5 - di - tert. - butyl - 4 - hydroxybenzoic acid(2,4-di-tert.-butyl)phenyl ester.
- B) 3,5 - di - tert. - butyl - 4 - hydroxybenzoic acid(4-tert.-octyl)phenyl ester.
- C) 3,5 - di - tert. - butyl - 4 - hydroxybenzoic acid(2,4-di-tert.-amyl)phenyl ester.
- 25 D) 3,5 - di - tert. - butyl - 4 - hydroxybenzoic acid(2-methyl-4-tert.-butyl)phenyl ester.
- E) 3,5 - di - tert. - butyl - 4 - hydroxybenzoic acid(2-tert.-butyl-4-methyl)phenyl ester.

Valuable 2-hydroxybenzophenones, usable 30 according to the invention, are, e.g.:

- F) 2-hydroxy-4-octyloxybenzophenone.
- G) 2-hydroxy-4-decyloxybenzophenone.
- H) 2-hydroxy-4-dodecyloxybenzophenone.

The production of the compounds of the 35 formulae I and II is described in the US Patents 3,112,338, 3,206,431, 3,006,959 and 3,098,842.

The carriers for the stabiliser system, 40 according to the invention, are polyolefins, both thermoplastic and cross-linkable polyolefins.

The polyolefins, suitable as carrier materials 45 for the stabiliser system, can be homo-polymers and copolymers which have been converted by radical, ionic or metallorganic polymerisation initiators into the corresponding polymers. Examples of monomers, the homo- and copolymerisates of which are suitable as carrier materials, are polymerisable 50 hydrocarbons with double bonds capable of addition, especially ethylene, propylene, 1-butene, methylpentene-1 and isobutylene, whereby optionally, both the atactic and the tactic polymerisation forms are suitable.

Particularly preferred are the homopolymers 55 of ethylene, propylene and butylene, as well as their copolymerisates.

The molecular weight of the above mentioned polyolefins is of secondary importance, 60 provided that it is within the required limits for the characteristic mechanical properties

of the respective polyolefins. Depending on the polyolefin, it can be 1000 to several millions. The incorporation of the stabiliser system, according to the invention, into the polymers is effected, e.g. by the stabiliser system and optionally further additives, e.g. softeners, antioxidants, metal-deactivators, other agents protecting against light rays, heat-stabilisers or pigments, being worked into the melt by methods common in the art, prior to or while shaping the polymeric articles, or by them being dissolved in the corresponding monomer before polymerisation, or by dissolving the polymer and the additives in solvents and subsequently evaporating the solvents.

Further suitable additives are, e.g.:

Antioxidants:

- a) phenolic compounds, e.g.
2,2' - thiobis - (4 - methyl - 6 - tert. - butylphenol); 4,4' - thiobis - (3 - methyl - 6 - tert. - butylphenol); 2,2' - methylene-bis - (4 - methyl - 6 - tert. - butylphenol); 2,2' - methylene - bis - (4 - ethyl - 6 - tert. - butylphenol); 4,4' - methylene - bis - (2 - methyl - 6 - tert. - butylphenol); 4,4' - butylidine - bis - (3 - methyl - 6 - tert. - butylphenol); 2,2' - methylene - bis - [4 - methyl - 6 - (α - methylcyclohexyl) - phenol]; 2,6 - di - (2' - hydroxy - 3' - tert. - butyl - 5' - methylbenzyl) - 4 - methylphenol; 1,1,3 - tris - (4' - hydroxy - 2' - methyl - 5' - tert. - butylphenyl) - butane; 1,3,5 - tri-methyl - 2,4,6 - tri - (3',5' - di-tert. - butyl - 4' - hydroxybenzyl) - benzene; esters of β - 4 - hydroxy - 3,5 - di-tert. - butylphenyl-propionic acid with mono- or polyvalent alcohols such as methanol, octadecanol, hexanediol, nonanediol, trimethylethane or pentaerythritol; 2,4 - bis - octyl - mercapto - 6 - (4 - hydroxy - 3,5 - di-tert. - butyl-anilino) - s - triazine; 2,4 - bis - (4 - hydroxy - 3,5 - di-tert. - butylphenoxy) - 6 - octyl - mercapto - s - triazine; 1,1 - bis - (4' - hydroxy - 2' - methyl - 5' - tert. - butyl) - phenyl - 3 - dodecylmercaptopbutane; 4 - hydroxy - 3,5 - di-tert. - butylbenzylphosphonic acid esters such as the diethyl or di-octadecyl ester; (3 - methyl - 4 - hydroxy - 5 - tert. - butylbenzyl) - malonic acid-di-octadecyl ester; S - (3,5 - dimethyl - 4 - hydroxybenzyl) - thioglycolic acid - octadecyl ester;
- b) 1,2-dihydroquinolines, e.g.
6 - ethoxy - 2,2,4 - trimethyl - 1,2 - dihydroquinoline; 6 - dodecyl - 2,2,4 - trimethyl - 1,2 - dihydroquinoline; polymerised 2,2,4 - trimethyl - 1,2 - dihydroquinoline.
- UV-absorbers and agents protecting against light rays such as:
a) 2,4 - bis - (2' - hydroxyphenyl) - 6 - alkyl - s - triazines such as the 6 - ethyl- or 6-undecyl derivative;
- b) Arylesters of optionally substituted benzoates, e.g. phenylsalicylate; octylphenyl-

- salicylates; benzoyl resorcin; dibenzoyl resorcin; α -cyano- β,β -diphenylacrylic acid-ethyl or isoctyl ester; α -carbomethoxy-cinnamic acid methyl ester; α -cyano- β -methyl-p-methoxycinnamic acid methyl or butyl ester;
- 5 c) Acrylates, e.g.
 N-(β -cyano- β -carbomethoxyvinyl)-2-methylindoline;
- 10 d) Nickel compounds, e.g.
 nickel complexes of the 2,2'-thiobis-(4-di-tert-octylphenol), such as the 1:1 and 2:1 complex, optionally with other ligands such as n-butylamine; nickel dibutylthiocarbamate; the nickel complex of 2-hydroxy-4-methylacetophenoneoxime or of 2-hydroxy-4-methylphenylundecyl ketone oxime;
- 15 e) Oxanilides, e.g.
 4,4'-di-octyloxy-oxanilide; 2,2'-di-octyloxy-5,5'-di-tert.-butyloxanilide;
- 20 2,2'-di-dodecyloxy-5,5'-di-tert.-butyloxanilide.
- Metal deactivators:
 mono- and dihydrazides of mono- and polybasic acids such as the oxalic, adipic, salicylic, terephthalic or isophthalic acid; substituted oxamides and oxanilides; N-salicyloyl-salicyl-aldehyde hydrazones; n-butylbenzotriazole; tetrahydrobenzotriazole; 2-guanidinobenzimidazole.
- 25 30 Nucleating agents:
 4-tert.-butylbenzoic acid, adipic acid, diphenylacetic acid.
- Peroxide-decomposers:
 esters of the β -thiodipropionic acid, e.g. the lauryl, stearyl, myristyl or tridecyl ester;
- 35
- salts of 2-mercaptopbenzimidazole, e.g. the zinc salt; phosphites such as triphenyl phosphite; diphenylalkyl phosphites; phenyldialkyl phosphites; trinonylphenyl phosphite; triauryl phosphite; trioctadecyl phosphite; 3,9-diisooctyloxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro-(5,5)-undecane; tri-(4-hydroxy-3,5-ditert.-butylphenyl) phosphite.
- 40 Other additives such as softeners, antistatic agents, flameproofing agents, pigments, soot. Inorganic fillers, e.g. asbestos, glass fibres, kaolin, talcum.
- The stabiliser system can also be applied from baths, e.g. from aqueous dispersions or from solutions in organic solvents, to polyolefin granulate or to carrier structures such as films, threads, split-fibres, slit films or sheets.
- The following Examples illustrate the present invention. The definitions of the letters A to H in Tables II, III and IV are the same as hereinbefore listed.
- 45
- 50 Example 1.
- 55 60 100 parts of polypropylene are mixed homogeneously, in the Brabender Plastograph, with 0.2 parts of 3,5-ditert.-butyl-4-hydroxybenzyl-phosphonic acid dioctadecyl ester and with the stabilisers given in Table I at 200° C. The thus obtained mixture is pressed to form 100 mil thick sheets. These sheets were exposed for 100 hours in a fluorescent sunlamp/black-light exposure apparatus. The degree of discolouration thereby occurring was visually assessed by comparison with the unexposed sheets. The results are shown in Table I.
- 65
- 70

TABLE I

Specimen	Stabiliser	Unexposed	Exposed
I	0.5% of 3,5-ditert.-butyl-4-hydroxybenzoic acid (2,4-di-tert.-butyl)phenyl ester	colourless	yellowish
II	0.4% of 3,5-di-tert.butyl-4-hydroxybenzoic acid (2,4-di-tert.-butyl)phenyl ester + 0.1% of 2-hydroxy-4-octyloxybenzophenone	colourless	slightly yellowish
III	0.25% of 3,5-di-tert.butyl-4-hydroxybenzoic acid (2,4-di-tert.-butyl)phenyl ester 0.25% of 2-hydroxy-4-octyloxybenzophenone	colourless	colourless

Example 2.

1000 parts of polypropylene powder (melt index 2.5) are mixed for 30 minutes in a drum mixer with 1 part of β -(3,5-ditert.-butyl-4-hydroxyphenyl)propionic acid octa-

decyl ester and the stabiliser system given in Table II and subsequently granulated in a Buss-Kokneter at 200° C. The obtained granulate is processed in the usual manner through an extruder having a slot die into a

75 80

film which, after being cut into strips, is stretched in the ratio of 1:6 and then coiled. (Denier of the strips: 700—900 den, tensile strength 5.5—6.5 g/den). The thus produced polypropylene strips are mounted, without stress, on to specimen carriers and exposed in the Xenotest apparatus. After varying times, 5 strips are removed each time and their tensile strength determined. As a measure of the effectiveness of the respective stabiliser system, the exposure time is given after which the tensile strength of the specimens has fallen to half the initial value. The obtained values are listed in Table II. The letters A—H in this Table refer to the stabilizers hereinbefore listed under these letters.

10

15

TABLE II

Mixture	Stabiliser system	No. of hours for the tensile strength to fall to 50% of the initial value
1	without stabiliser	310
2	0.25% A	1040
3	0.25% F	460
4	0.25% G	450
5	0.25% H	480
6	0.5% A	1470
7	0.5% F	690
8	0.5% G	680
9	0.5% H	700
10	0.25% A + 0.25% F	1390
11	0.25% A + 0.25% G	1350
12	0.25% A + 0.25% H	1380
13	0.1% A + 0.4% F	1000
14	0.4% A + 0.1% F	1450
15	0.3% A + 0.2% H	1410
16	0.2% A + 0.3% G	1260
17	0.125% A + 0.125% F	900
18	0.125% A + 0.125% H	920
19	0.05% A + 0.2% F	670
20	0.2% A + 0.05% G	1000
21	0.25% B + 0.25% F	1340
22	0.25% C + 0.25% F	1350
23	0.25% D + 0.25% F	1380
24	0.25% E + 0.25% F	1380

Example 3.

1000 parts of polypropylene powder (melting index 2.3) are mixed for 30 minutes in a drum mixer with 1 part of the pentaacrylthriol β -(3,5-ditert.-butyl-4-hydroxyphenyl)-propionic acid tetraester, 15 parts of titanium dioxide and the stabiliser system given in Table III and subsequently processed into polypropylene strips, as described in ex-

ample 2. The thus produced polypropylene strips were mounted, free from stress, on to specimen carriers and exposed in the Xenotest apparatus. Their tensile strength was determined after 900 hours exposure time. In Table III, the measured tensile strength values are given in % of the value before exposure. The letters in this Table refer to the stabilizers listed under these letters on page 5.

TABLE III

Mixture	Stabiliser system	Tensile strength after 900 hours exposure
1	without light stabiliser	<10%
2	0.5% A	85%
3	0.5% F	36%
4	0.25% A + 0.25% F	80%

Example 4.

1000 parts of polypropylene powder are homogeneously mixed in the Brabender Plastograph at 200°C with 2 parts of β -(3,5-ditert.-butyl-4-hydroxyphenyl)-propionic acid octadecyl ester and with the stabilisers given in Table IV, and then pressed in a platen press, at 260°C/6 min., to form 1 mm thick

sheets. These pressed sheets were stored at room temperature, suspended in air, and a visual assessment of the degree of exudation of the additives was made after 7 days and after 20 days. The results are listed in Table IV. The letters in this Table refer to the stabilizers hereinbefore listed under these letters.

10

15

30

35

TABLE IV

Stabilisers	Visual assessment after	
	7 days	20 days
1% A	slight exudation	strong exudation
0.5% A + 0.5% F	fully compatible	commencing exudation
0.5% A + 0.5% H	"	"
0.5% A	fully compatible	commencing exudation
0.25% A + 0.25% F	"	fully compatible
0.25% A + 0.25% H	"	"

Good results are also obtained when 3,5-di-tert.-butyl-4-hydroxybenzoic acid (2,4-di-tert.-amyl) phenyl ester and 2-hydroxy-4-dodecyloxybenzophenone are incorporated.

WHAT WE CLAIM IS:—

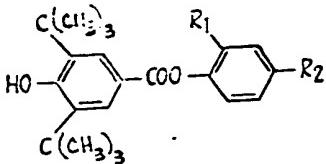
- A method of stabilising light-sensitive

polyolefins, which method comprises incorporating into the polyolefin, in a total amount from 0.2% to 1.2% by weight of the unstabilised polyolefin;

i) from 0.05% to 0.8% by weight of the unstabilised polyolefin of a compound of the formula:

45

50



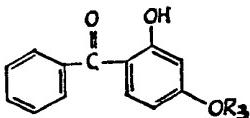
wherein:

R₁ represents a hydrogen atom or a methyl, tert.-butyl or tert.-amyl group; and

5 R₂ represents a methyl, tert.-butyl, tert.-amyl or tert.-octyl group,

R₁ and R₂ together containing at least 5 carbon atoms; and

10 ii) from 0.05% to 0.8% by weight of the unstabilised polyolefin of a compound of the formula:



wherein:

R₃ represents a C₈ to C₁₂ alkyl group.

15 2. A method according to claim 1 wherein R₃ represents an octyl, decyl or dodecyl group.

2. A method according to claim 1 wherein the polyolefin is polypropylene.

20 3. A method according to claim 1 or 2 wherein 0.05 to 0.5% by weight of a compound of the formula I and 0.1 to 0.8% by weight of a compound of the formula II are incorporated.

25 4. A method according to claim 1 or 2 wherein 0.05 to 0.25% by weight of a compound of the formula I and 0.2 to 0.5% by weight of a compound of the formula II are incorporated.

30 5. A method according to any of claims 1—4 wherein the total concentration of the compounds of the formulae I and II amounts to 0.2 to 0.8% by weight.

35 6. A method according to any of claims 1—4 wherein the total concentration of the compounds of the formulae I and II amounts to 0.2 to 0.5% by weight.

40 7. A method according to any of claims 1—6 wherein 3,5-di-tert.-butyl-4-hydroxybenzoic acid (2,4-di-tert.-butyl)phenyl ester and 2-hydroxy-4-octyloxybenzophenone are incorporated.

8. A method according to any of claims 1—6 wherein 3,5-di-tert.-butyl-4-hydroxybenzoic acid (2,4-di-tert.-butyl)phenyl ester and 2-hydroxy-4-decyloxybenzophenone are incorporated.

45 9. A method according to any of claims 1—6 wherein 3,5-di-tert.-butyl-4-hydroxybenzoic acid (2,4-di-tert.-butyl)phenyl ester and 2-hydroxy-4-dodecyloxybenzophenone are incorporated.

50 10. A method according to any of claims 1—6 wherein 3,5-di-tert.-butyl-4-hydroxybenzoic acid (4-tert.-octyl)phenyl ester and 2-hydroxy-4-octyloxybenzophenone are incorporated.

55 11. A method according to any of claims 1—6 wherein 3,5-di-tert.-butyl-4-hydroxybenzoic acid (2,4-di-tert.-amyl)phenyl ester and 2-hydroxy-4-dodecyloxybenzophenone are incorporated.

12. A composition of matter produced according to claim 1.

13. A composition of matter produced according to claim 2.

14. A composition of matter produced according to claim 3.

15. A composition of matter produced according to claim 4.

16. A composition of matter produced according to claim 5.

17. A composition of matter produced according to claim 6.

18. A composition of matter produced according to claim 7.

19. A composition of matter produced according to claim 8.

20. A composition of matter produced according to claim 9.

21. A composition of matter produced according to claim 10.

22. A composition of matter produced according to claim 11.

23. A method according to claim 1 substantially as described with reference to any one of the foregoing specific Examples 1—4.

24. A composition of matter produced by a process according to claim 23.

Agents for the Applicants,
GALLAFENT & CO.,
Chartered Patent Agents,
8, Staple Inn, London, WC1V 7QH.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1973.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.